I. THE USE OF ZEOLITE MATERIAL FOR THE IMPROVEMENT OF SUGAR SIRUPS.

II. A CRITICAL EXAMINATION OF THE METHODS FOR THE DETERMINATION OF LEVULOSE IN NATURAL PRODUCTS.

BY

WILLIAM JOHN SHANNON

B.A., University of Illinois, 1936
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SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
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PART I

THE USE OF ZEOLITE MATERIAL FOR THE IMPROVEMENT OF SUGAR SIRUPS

INTRODUCTION

The production of a palatable sirup by direct hydrolysis of the aqueous extract of Jerusalem artichokes has been extensively studied.[3] This extract possessed a very high buffer capacity due to the presence of potassium salts of organic acids,[5] and the concentration of acid required to effect hydrolysis was therefore relatively large. However, the amount of acid added must be kept at a minimum or its subsequent neutralization, with the formation of large amounts of salts, would impair, if not ruin, the palatability of the product. The use of a strong acid whose anion will form a relatively insoluble salt upon neutralization with a suitable base has been given some preliminary consideration.[3] The use of sulfuric acid followed by neutralization with calcium hydroxide offers the greatest promise. But small amounts of soluble calcium salts impart a bitter taste to food products and a substitution of the residual calcium ion by some less objectionable cation is desired. Of the cations permissible, sodium is probably the best.

One method of replacing calcium ion with sodium ion is by the use of base-exchange material.[7] In this investigation the principal objectives were: a) The study of the effect of a pure sugar sirup on the zeolite material used; b) the study of the effect of zeolite treatment upon the inorganic constituents of natural sugar products such as molasses, sorghum, and artichoke sirup.

Doucil, a product of the American Doucil Company, was selected for the investigation of the possibilities in using a base-exchange material for the improvement of natural sugar sirups because of its ready availability and its high base-exchange capacity.

EXPERIMENTAL RESULTS

1. The solvent action of pure sugar solutions upon Doucil, a synthetic base-exchange material, was investigated and found to be negligible.

2. A study of the base-exchange reaction showed that the hydrogen ion concentration of those solutions treated decreased on passage through the zeolite column.

3. Although the manufacturers of Doucil do not recommend its use at elevated temperatures, the results obtained here indicate that it may be used for the treatment of sugar solutions in a temperature range of 30 to 60° C.

4. Sorghum sirups were subjected to the base-exchange treatment and the ash from the treated and untreated samples analyzed. Data indicated that a satisfactory exchange of potassium and calcium ions from the sorghum sirup for sodium ions of the zeolite material had been made.

5. In view of the successful treatment of sorghum samples, sirups were prepared from dried Jerusalem artichoke chips and subjected to a carefully regulated base-exchange treatment. When these sirups were compared to ordinary artichoke sirups, prepared at the same time, they were found to possess a superior flavor. Analysis of the ash from these sirups showed an adequate exchange between sodium and potassium ions, but the calcium content of the treated sample had not been greatly reduced.

6. Attempts to reduce the calcium content of artichoke sirups by repeated treatment with zeolite were unsuccessful; furthermore, the R_2O_3 group increased slowly, indicating a slight solvent action on the Doucil.

PART II

A CRITICAL EXAMINATION OF THE METHODS FOR THE DETERMINATION OF LEVULOSE IN NATURAL PRODUCTS

INTRODUCTION

The scientific trend of the food industries and the necessity for the chemist to know the composition of his products in greater detail has given rise to a large number of sugar methods. In former years the sugar analyst was content to run determinations of reducing and non-reducing sugars on his products with little concern for the individual constituents present. Today, however, with the increased use of various carbohydrate materials in food preparation, the chemist has been forced to develop methods which will differentiate between the individual sugars.

The ketose sugar, levulose, promises to assume a very important role in the carbohydrate studies of the future. The juices contained in the roots of the Jerusalem artichoke, dahlia, chicory and many other composite flowering plants are rich in polysaccharides of which levulose is the predominate sugar. When it occurs as the free sugar, it is invariably accompanied by dextrose and frequently by sucrose or other sugars. Hence, as a final step in the analysis of a natural product where the carbohydrates have been converted to their simplest units, one is always confronted with the problem of determining each of these sugars in the presence of the others.

In the final analysis, the test of a good method for the determination of levulose seems to involve a comparison of results obtained by that method with results obtained by all approved methods when portions of the same samples, which have been derived from as many sources as possible are analyzed.

It was the purpose of this study: a) To examine the alkaline ferricyanide procedure developed by Becker and to learn if any further improvements could be made at any stage of the process; b) to compare the results of the determination of levulose by the selective ferricyanide method with those of other methods, especially the method of Nyns[3] as improved by Jackson and Mathews[4]; c) to establish the characteristics of the ferricyanide reagent when used at boiling temperature for the determination of total reducing sugars and the effect of the presence of sucrose upon this reaction.

EXPERIMENTAL RESULTS

1. The alkaline ferricyanide method of determining levulose as outlined by Becker[1,2] was confirmed. The following modifications in technique were made: the size of the reaction container was changed from a 125 to a 200 c.c. Erlenmeyer flask; a blank determination was carried out concurrently with the analysis of sugar mixtures; it was found advantageous to adopt the standardized technique of cooling the reaction flask and contents in an ice water bath for one minute before neutralization.

2. Attempts to alter the selectivity of the alkaline ferricyanide reagent towards levulose as contrasted with dextrose were made. Substitution of potassium salts in equal molar concentration for the sodium salts of the reagent failed to increase the differential reducing action of the two sugars. Neither the presence of sodium molybdate nor osmic acid in small amounts showed the expected catalytic effect.

3. It has been established that the determination of reducing sugars employing the same alkaline ferricyanide reagent which was used to determine levulose in the presence of dextrose may be accomplished by carrying out the reaction at a higher temperature for a shorter period of time. The presence of large amounts of sucrose showed no effect on the reaction.

4. The addition of a large amount of sodium hydrogen phosphate to the standard Nyns reagent[8] produced no increase in its selectivity.

5. The levulose content of natural products, including artichoke sirups, sorghum sirup, chicory extract, and honey was determined by each of the following methods: alkaline ferricyanide,[1] carbonate-bicarbonate copper,[4] and double temperature polarization,[4] as well as by difference using the alkaline iodine oxidation of dextrose.[6] The alkaline ferricyanide method was found to be superior to the other methods because it required a shorter time to carry out and was more convenient to handle.

BIBLIOGRAPHY

[1] Becker, H., Doctor's Dissertation, U. of Ill. (1940).

[2] Becker, H., and Englis, D. T., Ind. Eng. Chem., Anal. Ed. **11**, 145 (1939).

[3] Englis, D. T., and Coworkers, Ind. Eng. Chem. **25**, 937 (1933).

[4] Jackson, R. F., and Mathews, J. A., Bur. Standards J. Research **8**, 404 (1932).

[5] Jackson, R. F., Mathews, J. A., and Chase, W. D., Bur. Standards J. Research **9**, 493 (1932).

[6] Kolthoff, I. M., "Volumetric Analysis," Vol. II, p. 446. Wiley, 1929.

[7] Larson, R., B.S. Thesis, U. of Ill. (1937).

[8] Nyns, L., Sucr. belge **44**, 210 (1924).

VITA

The author was born in Ottawa, Ontario, Canada, on March 9, 1912. He attended the public schools in Ontario until December, 1923, at which time he moved to Joliet, Illinois, and there completed his elementary education. He was graduated from the Joliet Township High School in 1930 and from the Joliet Junior College in 1932. In 1934 he enrolled in the University of Illinois and completed the requirements for a B.A. degree in 1936 with Honors in Chemistry. The degree of Master of Science was granted him in 1938. From September, 1936, through June, 1940, he held a teaching assistantship in the chemistry department at the University of Illinois.

He is a member of the American Chemical Society, The Chemist's Club of New York City, Sigma Xi, Phi Lambda Upsilon, and Phi Beta Kappa.

PUBLICATIONS

1. Englis, D. T., and Shannon, W. J., "Cleaning of Whole-Kernel Corn." Canner 82 (No. 23), 14 (1936).
2. Shannon, W. J., and Englis, D. T., "Copper in Tomatoes." J. Assoc. Official Agr. Chem. 23, 678 (1940).